

**Water Rock Interaction [WRI 14]****Geochemical comparison of high and low arsenic groundwater in the Hetao Basin, Inner Mongolia**Huaming Guo^{*, a, b}, Zhaoli Shen^b, Yang Zhang^a, Yongfeng Jia^{a, b}, Kai Zhao^{a, b}^a State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Beijing 100083, P.R. China^b School of Water Resources and Environment, China University of Geosciences (Beijing), Beijing 100083, P.R. China**Abstract**

Four multilevel samplers were installed in both As-affected areas and low-As areas for long-term monitoring of chemical variations of shallow groundwater (< 30 m in depth). Results showed slight increasing trends in As concentrations in groundwaters with high As concentration (> 50 µg/L), and in groundwaters at 15 m depth in low-As areas. Variations in As concentrations were in line with those of Fe(II) in low-As areas (< 50 µg/L), while incompatible variations were generally observed in groundwaters from As-affected areas. This indicated that authigenic siderite and pyrite immobilized As in groundwaters with high As concentration (>200 µg/L), being released from aquifer sediments via reductive dissolution of Fe oxides.

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Keywords: As species; China; Hydrogeochemistry; Water-Rock Interaction**1. Introduction**

High As groundwater has received serious concern from scientific community and water management agencies [1-3]. Reducing aquifers have been found to host high As groundwaters in major river deltas of SE Asia such as Red River delta, Mekong delta, Ganges delta, Yellow river delta, Pearl River delta [1-3] and inland basins for example the Hetao basin, the Datong basin, the Yinchuan basin, the west Jilin basin, and Zhunger basin [4-7]. Unpredicted patterns of spatial and temporal variations are the universal characteristics of groundwater As in those aquifers of river deltas and inland basins [1-5].

The Hetao basin is a typical inland basin hosting high As groundwater in shallow aquifers (0.6-572 µg/L) [4]. Spatial distribution of groundwater As has been well documented [4-7], showing the patchy

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distribution of As concentration at both local (~100 m) and regional scales (~10 km) [4]. However, few data are available on temporal variation in groundwater As concentration. Limited data showed that groundwater As concentration is mostly higher at the time of high groundwater level (< 1.0 m below land surface) [7]. Comparison of hydrogeochemical temporal variations between high As groundwater (> 50 µg/L As) and low As groundwater would help in effectively managing groundwater resources for ensuring drinking water safety and in better understanding mechanisms of As mobilization in the shallow aquifers.

The major objectives are to (1) characterize geochemistry of high and low As groundwater, (2) to investigate temporal variations in groundwater chemistry in high and low As aquifers, and (3) to evaluate hydrogeochemical processes controlling groundwater As concentrations.

2. Materials and Methods

Four multilevel samplers were installed in the Shahai town, two of which are located in the regions with high As groundwater (BH01 and BH04), and two in the regions with low As groundwater (BH02 and BH03) (Fig.1). Depths of samplers and lithologic settings were provided in Guo et al. [6]. Groundwater was sampled from each sampler after pumping (usually 20 min). All of samples were filtered through 0.45 µm membrane filters in the field for analysis in the laboratory [5].

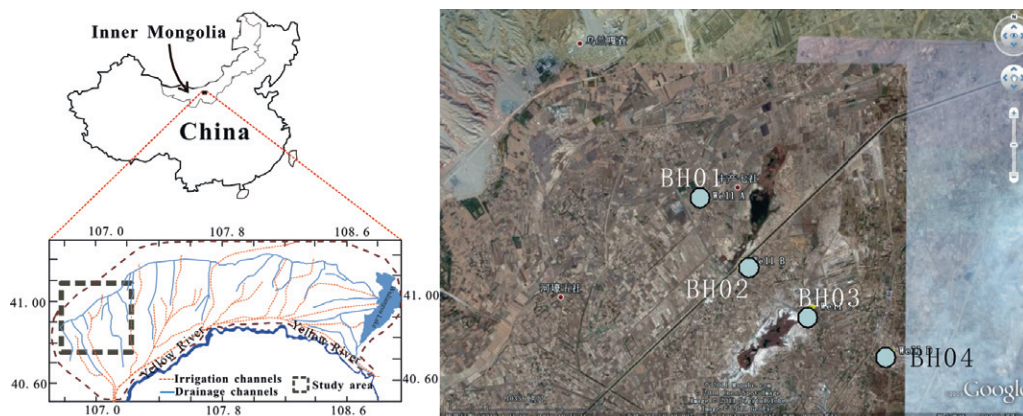


Fig. 1. Location of multilevel samplers in the study area

3. Results and Discussion

3.1. Chemical characteristics of high and low As groundwaters

Groundwater had neutral-weak alkaline pH, with the range between 7.25 and 8.54. Eh values lay between 28.5 and 246 mV. Total dissolved solids (TDS) ranged between 745 and 5280 mg/L, showing increasing trends with depth. The highest TDS value was found at BH03, which is the discharge area of local groundwater flow system. Evaporation is the major process controlling groundwater chemistry at BH02 and BH03, evidenced by the enrichment in ^{18}O and D.

High As concentration was found in BH01 and BH04, with the levels between 220 and 625 µg/L (median 331 µg/L), while low As concentration in BH02 and BH03 with As concentrations between 0.4 and 113 µg/L (20.3 µg/L). Arsenic (III) accounted for 60 % - 99 % of total As in water samples with total As > 20 µg/L. For both low and high As groundwater, water type is mainly Na-HCO₃-Cl/Na-Cl-HCO₃.

Sodium and HCO_3/Cl are the predominant components in cation and anion, respectively. Ammonia and H_2S were detected in the waters. In sites BH01 and BH04, $\text{NH}_4\text{-N}$ concentrations ranged between 3.1 and 6.0 mg/L (median 4.0 mg/L). In sites BH02 and BH03, its range lay between 0.15 and 4.25 mg/L (median 1.3 mg/L). Sulfide concentrations had the range of 0.1 to 17 $\mu\text{g/L}$, with the greater values in groundwaters of BH04. Iron(II) concentrations (1.0–4.7 mg/L) were generally higher in BH01 than those in BH02 and BH03 (0.1–2.7 mg/L), which are consistent with higher As concentration in BH01 than in BH02 and BH03. Although high As concentration was found in BH04, Fe(II) concentration was quite low, ranging between 0.08 and 0.45 mg/L. Sulfate concentration ranged between < 0.1 and 792 mg/L in BH01 (averagely 379 mg/L), which is much higher than in BH04 (< 0.1–16 mg/L). Sulfate concentrations in BH02 and BH03 were between 43 and 499 mg/L.

Generally, As concentration, $\text{NH}_4\text{-N}$, and Fe(II) increased with increasing sampling depths < 20 m at the same site. However, Eh, TDS and F concentrations had decreasing trends with the sampling depths (< 20 m). For BH02, Eh decreased from 138 mV at the depth of 9.5 m to 73 mV at the depth of 20 m in November 2010, while total As concentration increased from 4.3 to 95 $\mu\text{g/L}$ possibly due to the shift of redox conditions.

3.2. Temporal variation in As concentrations of high and low As groundwaters

Generally, As concentration showed temporal variation at all locations during 18 months. In the Sites BH01 and BH04 with high As groundwaters, As concentrations generally showed slight increasing trends, although a slight decrease was observed from October 28, 2011 to April 27, 2012 (Fig.2). The fluctuation in As concentration possible related to water level changes [7]. Generally, groundwater has higher As concentration in irrigation seasons, in comparison with that in winter time (November–April). The increasing trends were also found in groundwaters at depths of 15 m at Sites BH02 and Bh03. However, As concentration kept relatively constant at depths less than 10 m, where low As groundwaters were present (< 10 $\mu\text{g/L}$). At 20 m depth of those sites, groundwater showed slight decreasing trends in As concentration (data not shown). In comparison with As variation, groundwater Eh generally showed opposite variation trends, generally showing decreasing trends.

Iron(II) showed different variation trends from As concentrations. In groundwaters with As concentrations less than 100 $\mu\text{g/L}$ at BH02 and BH03, Fe(II) variations were in line with those in As variations. However, at depths of 20 m at BH01, BH02 and BH04 and of 15 m of BH01 with As concentration > 100 $\mu\text{g/L}$, Fe(II) had distinct variation trends from As at depths, possibly indicated controls of S^{2-} on As and Fe(II) cycling.

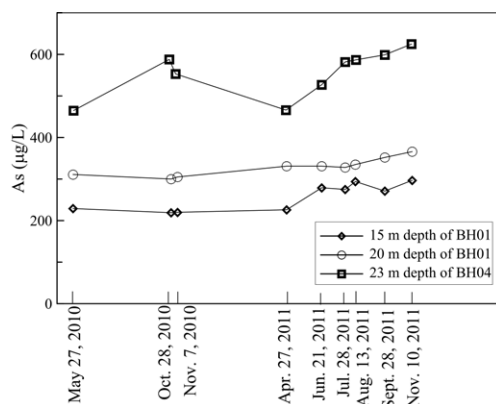


Fig. 2. Temporal variations in As concentrations of groundwaters from BH01 and BH04

3.3. Controls of As concentration

There was a negative correlation between As and Eh. Arsenic concentrations were generally high ($> 100 \mu\text{g/L}$) in reducing groundwaters with Eh less than 100 mV. Reducing conditions was the predominant factor controlling As mobilization in the aquifers, which is in agreement with others in the river deltas and inland basin [1-7]. Arsenic was believed to be released into groundwater from aquifer sediments under reducing condition via reductive reduction of Fe(III) oxide minerals, which was supported by the similar change trends in As and Fe(II) concentration at BH02 and BH03.

In reducing conditions, it was observed that As was poorly correlated with Fe(II) at BH01 and BH04. Observation of temporal variations also showed the incompatible trends between As and Fe(II) in groundwaters with As $> 100 \mu\text{g/L}$. Typically, low Fe(II) was detected in groundwater of BH04, where high As concentrations occurred in reducing conditions. It indicated that Fe(II) mineral precipitation would attribute to this observation. Results of saturation index calculation showed high As groundwaters were oversaturated with regard to siderite and pyrite (data not shown). There were negative correlations between As concentration and $\text{SI}_{\text{siderite}}$ and $\text{SI}_{\text{pyrite}}$. In these groundwaters with high SI values, groundwater As concentrations were generally low. It indicated the controls of siderite and pyrite precipitations on groundwater As. Siderite was found to host substantial As in both laboratory condition and the field site [8]. The formation of authigenic pyrite was proposed to be the sink of groundwater As by co-precipitation in strongly reducing environments [9].

Acknowledgements

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